



INVESTOR IN PEOPLE

The Patent Office
Concept House
Cardiff Road
Newport
South Wales
NP10 8QQ

REC'D 17 AUG 2004

WIPO

PCT

I, the undersigned, being an officer duly authorised in accordance with Section 74(1) and (4) of the Deregulation & Contracting Out Act 1994, to sign and issue certificates on behalf of the Comptroller-General, hereby certify that annexed hereto is a true copy of the documents as originally filed in connection with the patent application identified therein.

In accordance with the Patents (Companies Re-registration) Rules 1982, if a company named in this certificate and any accompanying documents has re-registered under the Companies Act 1980 with the same name as that with which it was registered immediately before re-registration save for the substitution as, or inclusion as, the last part of the name of the words "public limited company" or their equivalents in Welsh, references to the name of the company in this certificate and any accompanying documents shall be treated as references to the name with which it is so re-registered.

In accordance with the rules, the words "public limited company" may be replaced by p.l.c., plc, P.L.C. or PLC.

Re-registration under the Companies Act does not constitute a new legal entity but merely subjects the company to certain additional company law rules.

Signed

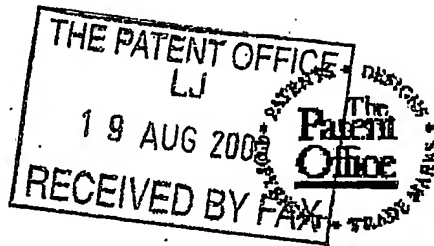
Dated

21 July 2004

**PRIORITY
DOCUMENT**

SUBMITTED OR TRANSMITTED IN
COMPLIANCE WITH RULE 17.1(a) OR (b)

Patents Form 1/77

Patents Act 1977
(Rule 16)19AUG03 E831434-1 D02813
P01/7700 0.00-0319455.2

1/77

Request for grant of a patent

(See the notes on the back of this form. You can also get an explanatory leaflet from the Patent Office to help you fill in this form)

The Patent Office

Cardiff Road
Newport
South Wales
NP10 8QQ

1.	Your Reference	P58939V-GB		
2.	Patent Application number (The Patent Office will fill in this part)	0319455.2		19 AUG 2003
3.	Full name, address and postcode of the or each applicant (underline all surnames)	The BOC Group plc Chertsey Road Windlesham Surrey GU20 6HJ		
	Patents ADP Number (if you know it)			
	If the applicant is a corporate body, give the country/state of its incorporation	United Kingdom		7975749001
4.	Title of the invention	Electrochemical Sensor		
5.	Name of your agent (if you have one)	FRY HEATH & SPENCE LLP		
	"Address for service" in the United Kingdom to which all correspondence should be sent (including the postcode)	The Gables Massetts Road Horley Surrey RH6 7DQ United Kingdom		
	Patents ADP Number (if you know it)	05880273001		8459554001
6.	If you are declaring priority from one or more earlier patent applications, give the country and the date of filing of the or each of these earlier applications and (if you know it) the or each application number.	Country	Priority application number (if you know it)	Date of filing (day / month / year)
7.	If this application is divided or otherwise derived from an earlier UK application, give the number and the filing date of the earlier application.	Number of earlier application		Date of filing (day / month / year)
8.	Is a statement of inventorship and of right to grant of a patent required in support of this request? (Answer 'Yes' if:	Yes		
	a) any applicant named in part 3 is not an inventor; or			
	b) there is an inventor who is not named as an applicant; or			
	c) applicant, or			
	d) any named applicant is a corporate body			
	(See note (d))			

Patents Form 1/77

9. Enter the number of sheets for any of the following items you are filing with this form. Do not count copies of the same document.

Continuation sheets of this form 0

Description 22

Claim(s) 8

Abstract 1

Drawing(s) 2

10. If you are also filing any of the following, state how many against each item.

Priority documents 0

Translations of priority documents 0

Statement of inventorship and right to grant of a patent (Patents Form 7/77) 0

Request for preliminary examination and search (Patents form 9/77) 1

Request for substantive examination (Patents form 10/77) 0

Any other documents (please specify) 0

11.

I/We request the grant of a patent on the basis of this application.

Signature

Date

D. Townsend

19 August 2003

12.

Name and daytime telephone number of person to contact in the United Kingdom

Victoria J Townsend - 01293 776880

Warning

After an application for a patent has been filed, the Comptroller of the Patent Office will consider whether publication or communication of the invention should be prohibited or restricted under Section 22 of the Patents Act 1977. You will be informed if it is necessary to prohibit or restrict your invention in this way. Furthermore, if you live in the United Kingdom, Section 23 of the Patents Act 1977 stops you filing or applying for a patent abroad without first getting written permission from the Patent Office unless an application has been filed at least 6 weeks beforehand in the United Kingdom for a patent for the same invention and either no direction prohibiting publication or communication has been given, or any such direction has been revoked.

Notes

- If you need help to fill in this form or you have any questions, please contact the Patent Office on 0645 500505.
- Write your answers in capital letters using black ink or you may type them.
- If there is not enough space for all the relevant details on any part of this form, please continue on a separate sheet of paper and write "see continuation sheet" in the relevant part(s). Any continuation sheet should be attached to this form.
- If you have answered 'Yes' Patents Form 7/77 will need to be filed.
- Once you have filled in the form you must remember to sign and date it.
- For details of the fee and ways to pay please contact the Patent Office.

DUPLICATE

1

Electrochemical Sensor

The current invention relates to sensors for the detection of organic contaminants in low oxygen concentration process environments such as those used in the semiconductor manufacturing industry, the use of such sensors and a novel method for the detection of organic contaminants in such process environments. By the term low oxygen concentration process environments it is to be understood to mean process environments in which the partial pressure of oxygen is of the order of 10^{-6} mb – 10^{-3} mb (parts per billion to parts per million).

In, for example, the semiconductor manufacturing industry, it is important to control the atmosphere (process environment) in which wafers are manufactured. The wafers are desirably manufactured in a controlled environment. Undesirable or varying levels of organic contaminants can result in device and/or equipment failure.

Levels of contaminating organic material in the parts per trillion (ppt) to parts per billion (ppb) range, which corresponds to a partial pressure of 10^{-9} to 10^{-6} mb do not, in general, result in equipment or device failure. However, if the levels of organic contaminants become much higher than this, failures may result. In order to control the process environment, it is necessary to monitor the levels of organic contaminants present. In particular, some processes are sensitive to contaminant material in the low ppb range, it is therefore desirable to monitor the level of contaminant materials in the ppt range for such processes. However, such monitoring processes are costly and it is difficult to determine an accurate value for the total organic compounds (TOC) present at such low contaminant levels. In addition, many fabrication processes are tolerant of light saturated hydrocarbons such as methane (CH_4) and ethane (C_2H_6), which have a particularly low reaction probabilities with most surfaces and therefore do not take part in the various contamination inducing reactions.

In vacuum based process environments, TOC levels are often determined using mass spectrometry. A mass spectrometer is capable of measuring contaminants present at ppt levels. However the interpretation of such measurements is often complicated by effects such as mass spectral overlap, molecular fragmentation and background effects, for example.

Although mass spectrometers can be used in process environments operating at ambient pressure or above, additional vacuum and sample handling systems are required, which make such instruments very expensive. Under such conditions, it is preferred to use Gas Chromatographic (GC) techniques to monitor the TOC levels present in the process environment. However, in order to monitor contaminants in the ppt range it is necessary to fit the gas chromatogram with a gas concentrator. Gas Chromatography technology can therefore be used to monitor TOC levels in the ppt range in Ultra High Purity (UHP) gas installations in semiconductor fabrication plants.

It should be noted that although Mass Spectrometry and Gas Chromatography are able to detect ppt levels of TOC, their ability to differentiate the presence of the process tolerant light hydrocarbons referred to above from the more harmful organic compounds is limited, which makes it difficult to determine the total levels of damaging hydrocarbons in the process environment.

In addition, because the use of either mass spectrometric or gas chromatographic techniques for determining the TOC levels present in process environments requires specialist equipment, they tend to be rather expensive and are typically only used as Point of Entry (POE) monitors for the whole facility rather than the more useful Point of Use (POU) monitors.

Hydrocarbons, including light hydrocarbons such as methane (CH_4) and ethane (C_2H_6), have been routinely monitored using common tin oxide (SnO_2) based sensor devices. These sensors typically operate under atmospheric pressure to detect target gases in the range from 10s of ppb (parts per billion) to several thousand ppm (parts per million). This type of sensor works effectively within these ranges by providing a linear output signal that is directly proportional to the quantity of target gas within the monitored environment. Although these sensors are suitable for monitoring contaminant levels within ambient environments, they do not lend themselves for applications with sub-atmospheric processing environments such as those encountered within semi-conductor processing environments. However, under such vacuum conditions the SnO_2 type of sensor (typically used for monitoring hydrocarbon levels in ambient) will suffer from reduction of the active oxide content leading to signal drift and non-response after a period of time.

Chemical sensors comprising solid state electrolytes such as oxygen anion conductors or silver or hydrogen cation conductors have been used to monitor levels of oxygen and carbon dioxide and hydrogen / carbon monoxide gas present in a process environment and are described in United Kingdom patent application number 0308939.8 and GB 2,348,006A, GB 2,119,933A respectively.

Such sensors are generally formed from an electrochemical cell comprising a measurement electrode, a reference electrode and a solid state electrolyte of a suitable ionic conductor disposed between and bridging said electrodes.

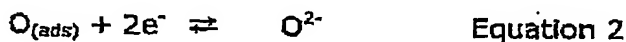
The gas monitor of GB 2,348,006A comprises a detection electrode containing a silver salt having an anion, which corresponds to the gas to be detected, a silver ion conducting solid state electrolyte and a reference silver electrode. The monitor can be used to detect gases such as carbon

dioxide, sulphur dioxide, sulphur trioxide, nitrogen oxides and halogens through the suitable choice of the appropriate anion.

For the oxygen sensors of United Kingdom patent application number 0308939.8, the solid state electrolyte conducts oxygen anions and the reference electrode is generally coated or formed from a catalyst, which is able to catalyse the dissociative adsorption of oxygen and is positioned within a reference environment, in which the concentration of oxygen adjacent the reference electrode remains constant.

Solid state oxygen anion conductors (solid state electrolytes) are generally formed from doped metal oxides such as gadolinium doped ceria or yttria stabilised zirconia (YSZ). At temperatures below the critical temperature for each electrolyte (T_c) the electrolyte material is non-conducting. At temperatures above T_c the electrolyte becomes progressively more conductive.

The levels of oxygen determined by such oxygen sensors in any monitored environment is determined by the electrochemical potentials generated by the reduction of oxygen gas at both the measurement and reference electrodes. The steps associated with the overall reduction reactions at each electrode are set out below, the half-cell reaction at each electrode being defined by equations 1 and 2 below.



The electrochemical potential generated at each electrode is determined by the Nernst equation:

$$E = E^{\ominus} + \frac{RT}{2F} \ln \frac{a(O_{ads})}{a(O^{2-})} \quad \text{Equation 3}$$

Where

E is the electrochemical half-cell potential at the reference or measurement electrode respectively;

E^{\ominus} is the standard electrochemical half cell potential of the cell at unit $O_{(ads)}$ activity

R is the gas constant

T is the temperature of the cell

F is Faraday's constant

$a(O_{ads})$ and $a(O^{2-})$ are the activities of the adsorbed oxygen at the electrode surface and reduced oxygen anion in the solid state ionic conductor respectively.

The activity of adsorbed oxygen at the electrode surface is directly proportional to the partial pressure of oxygen gas in the environment adjacent the electrode as defined by equation 4 below:

$$a_{O_{ads}} = K P_{O_2}^{1/2} \quad \text{Equation 4}$$

Since $a(O^{2-})$ is unity, by definition, and the activity of the adsorbed oxygen at the electrode surface is proportional to the partial pressure of the oxygen in the environment adjacent the electrode surface (Equation 4), the half cell potential can be written in terms of the partial pressure of oxygen in the particular environment adjacent the measurement or reference electrode respectively (Equation 5).

$$E = E^{\ominus} + \frac{RT}{4F} \ln P_{O_2} \quad \text{Equation 5}$$

Where

E is the electrochemical half-cell potential at the reference or measurement electrode respectively;

E° is the standard electrochemical half cell potential of the cell for oxygen at atmospheric pressure i.e. unit activity;

R is the gas constant

T is the temperature of the cell

F is Faraday's constant; and

$P(O_2)$ is the partial pressure of oxygen gas in the environment adjacent the electrode surface.

The potential difference V generated across the cell is defined in terms of the difference in the half-cell potentials between the reference and measurement electrodes in accordance with Equation 6.

$$V = E_{(R)} - E_{(M)} = \frac{RT}{4F} \ln \left(\frac{P_{O2(R)}}{P_{O2(M)}} \right) \quad \text{Equation 6}$$

Where

V is the potential difference across the cell

$E_{(R)}$ and $E_{(M)}$ are the electrochemical potentials at the reference and measurement electrodes respectively;

R , T and F are as defined above; and

$P_{O2(R)}$ and $P_{O2(M)}$ are the partial pressures of oxygen at the reference and measurement electrodes respectively.

Note that if both the reference and measurement electrodes are exposed to the same oxygen partial pressure e.g. atmospheric levels of oxygen, the potential difference across the cell is zero.

However, in process environments such as the oxygen deficient environments encountered in the manufacture of semi-conductor products

7

the partial pressure of oxygen adjacent the measurement electrode is considerably less than that adjacent the reference electrode. Since the electrochemical potential at each electrode is governed by the Nernst equation, as the partial pressures of oxygen at the measurement electrode decreases, the electrochemical potential at the measurement electrode changes, which results in the formation of a potential difference across the cell at temperatures above the critical temperature. The potential difference across the cell is determined by the ratio of the partial pressure of oxygen at the reference and measurement electrodes in accordance with equation 6 above. The oxygen sensor can therefore provide a user with an indication of the total amount of oxygen present in a monitored environment simply from determining the potential difference across the cell.

However, there is a need for a similar simple, low cost, semi-quantitative sensor, which has a low sensitivity to unreactive organic compounds but can be used at the point of use to analyse the process environment. The present invention addresses that need.

A first aspect of the present invention provides an organic contaminant molecule sensor, for use in a low oxygen concentration monitored environment the sensor comprising an electrochemical cell having:

a measurement electrode being coated with (or formed from) a catalyst having the ability to catalyse the dissociative adsorption of the organic contaminant molecule, the electrode being positioned for exposure to the monitored environment;

a reference electrode being coated with (or comprised from) a catalyst selected for its ability to catalyse the dissociation of oxygen to oxygen anions, the reference electrode being positioned within a reference environment;

a solid state oxygen anion conductor disposed between and bridging the measurement and reference electrodes, wherein oxygen anion conduction occurs at or above a critical temperature, T_c ;

means for controlling and monitoring the temperature of the cell, and sealing means for separating the reference environment from the monitored environment; and

means for controlling the electrical current (I_p) flowing between the reference and measurement electrodes

whereby at temperatures (T_{ads}) below the critical temperature, T_c , organic contaminant molecules are adsorbed onto and dissociated at the surface of the measurement electrode leading to the build up of carbonaceous deposits at the surface thereof and at temperatures (T_{dt}) above the critical temperature (T_c), an electrical current (I_p) is passed between the reference and measurement electrode thereby to control the number of oxygen anions passing from the reference electrode to the measurement electrode to oxidise the carbonaceous deposits formed at the surface thereof and the formation of carbon dioxide.

In the absence of organic contaminants, the potential difference across the cell V_0 at temperature, T_{dt} , and constant electrical current, I_p , is constant and is determined by the equilibrium between the flux of oxygen anions (O^{2-}) arriving at the electrode surface and the rate of desorption of oxygen gas ($O_{2(g)}$) from the electrode surface according to equations 1 and 2.

However, when carbonaceous deposits are present on the electrode surface they are oxidised (combusted) to carbon dioxide by the flux of oxygen anions arriving at the electrode surface. This has the effect of reducing the equilibrium concentration of oxygen anions (O^{2-}) at the surface which means that, in accordance with equation 3 above the potential across the cell, V_{dt} , is increased relative to V_0 .

However, when the current I_p is applied to the cell, oxygen anions are forced to flow from the reference electrode to the measurement electrode where they react with the carbonaceous deposits formed at the surface thereof during the adsorption phase, which results in the formation of carbon dioxide. As the carbonaceous deposits are transformed into carbon dioxide their concentration progressively decreases to zero at the surface of the measurement electrode and the concentration of oxygen at the surface of the measurement electrode will increase to the constant equilibrium value determined by the flux of oxygen anions to the electrode. The potential difference across the cell then returns to the constant value, V_o , and provides an indication that all the carbonaceous deposits on the surface of the electrodes have been removed.

The total amount of carbonaceous deposit formed at the surface of the measurement electrode can be determined by measuring the total amount of oxygen transported to the measurement electrode by the application of current I_p (which is required to oxidise all of the carbonaceous deposits) over the time t_p taken for the potential difference across the cell to return from V_{dt} to V_o . Since the transport of each oxygen anion to the surface of the measurement electrode requires the passage of two units of charge, the total quantity of oxygen atoms transported to the surface of the electrode is determined by the term:

$$\frac{I_p t_p}{2} \quad \text{Equation 7}$$

Since each atom of carbon deposited at the surface of the electrode requires two oxygen atoms for complete combustion, the total amount of carbon atoms oxidised during the titration phase and hence deposited at the electrode during the adsorption phase is:

10

$$\frac{I_p t_p}{4} \text{ Equation 8}$$

It will be appreciated that by controlling the time over which adsorption of the organic contaminants can occur on the surface of the measurement electrode, the value of the current I_p flowing between the reference and measurement electrodes at temperatures (T_{tit}) and the time t_p taken for the potential difference across the cell to drop from V_{tit} to V_o , it is possible to titrametrically monitor the levels of organic contaminants in the process environment in the parts per trillion (ppt) range or less. The sensor therefore provides a low cost alternative to the use of Mass Spectrometry and Gas Chromatography in the determination of low levels of organic impurities in process environments.

The reference environment may, for example, be a gaseous source of oxygen at constant pressure (such as atmospheric air) or a solid-state source of oxygen, typically a metal / metal oxide couple such as Cu / Cu₂O and Pd / PdO or a metal oxide / metal oxide couple such as Cu₂O / CuO.

The sensor is also easy to use and can be used at the point of use as well as the point of entry to provide accurate information about the process environments at all stages of the semi-conductor fabrication process.

The total level of contaminants measured by the sensor of the first aspect of the invention provides a semi-quantitative indication of the level of harmful organic contaminants present in the process environment. The non-contaminating light organic molecules present in the process environment do not stick to the surface of the measurement electrode and are not therefore measured. It is only the harmful organic contaminants, which have a high reaction probability with the electrode surface (and therefore with other surfaces encountered in the fabrication process) that undergo dissociation and are therefore subsequently oxidised at the

measurement electrode surface that are detected and therefore monitored by the measurement electrode.

Careful choice of the coating applied to the measurement electrode or the material from which it is formed will cause some of the harmful organic contaminants to adsorb onto the surface of the measurement electrode in preference to others. Preferably the measurement electrode is formed from material whose uptake of organic material proceeds with a sticking probability of or about unity. In addition the organic material is preferably efficiently adsorbed and cracked by electrode material. Further, the measurement electrode is suitably able to catalyse the dehydrogenation and cracking of organic contaminants. Suitable electrode materials include metals selected from the group comprising rhenium, osmium, iridium, ruthenium, rhodium, platinum and palladium and alloys thereof. Alloys of the aforementioned materials with silver, gold and copper may also be used.

The sensor according to the first aspect of the invention is easily and readily manufactured using techniques known to a person skilled in the art. Sensing, reference and optionally counter electrodes are applied to a thimble of an oxygen anion conductor solid state electrolyte such as yttria stabilised zirconia either in the form of an ink or a paint or using techniques such as sputtering. The sensing electrode is isolated from the reference and optionally counter electrode via the formation of a gas tight seal. The sensor suitably supplied with heater means to control the temperature of the electrolyte and means to monitor the voltage between the sensing electrode and the reference and counter electrodes respectively.

The reference electrode is suitably formed from materials, which are able to catalyse the dissociation of oxygen in the reference environment, typically Platinum is used. The reference environment can be derived from a gaseous or solid-state source of oxygen. Typically

atmospheric air is used as a gaseous reference source of oxygen although other gas compositions can be used. Solid-state sources of oxygen typically comprise of a metal / metal oxide couple such as Cu / Cu₂O and Pd / PdO or a metal oxide / metal oxide couple such as Cu₂O / CuO. The particular solid-state reference materials chosen will depend on the operating environment of the sensor and in particular the titration temperature T_{tit} . The solid state electrolyte comprising an oxygen anion conductor is suitably formed from a material, which exhibits oxygen anion conduction at temperatures above 300°C. Suitable oxygen anion conductors include gadolinium doped ceria and yttria stabilised zirconia. Preferred materials for use as the solid state oxygen anion conductor include 8% molar yttria stabilised zirconia (YSZ), which is commercially available.

A radiative heater is suitably used to control the temperature of the cell. Such heaters include heating filaments, wound around the solid state electrolyte. An electric light bulb can also be used.

A thermocouple is suitably used to monitor the temperature of the cell.

Currents of between 100nA and 100 μ A are suitably used for driving oxygen anions between the reference and measurement electrodes. Currents outside this range can be used, depending upon the circumstances. The magnitude of the current used to drive the oxygen anions between the reference and measurement electrodes depends upon the surface area of the electrode and the amount of cracked hydrocarbon deposited at the surface thereof. Larger currents will generally be required for electrodes having a greater surface area or a large amount of cracked hydrocarbon deposited on the surface thereof. The sensor is preferably used in conjunction with a device for measuring the potential (Electromotive Force, EMF) produced across the cell.

In use, the sensor continuously cycles between an adsorption mode and an oxygen titration mode:

In the adsorption mode, the sensor is held at a constant temperature, T_{ads} , which is below the critical temperature, T_c , for oxygen anion conduction within the solid state electrolyte. The T_c for YSZ, for example, is in the range 300°C . T_{ads} and the sensing electrode material are chosen such that the catalytic properties of the sensing electrode, at T_{ads} , cause adsorbed organic material to de-hydrogenate / crack leading to the build up of carbonaceous deposits on the surface. For a Platinum electrode, for example, T_{ads} is in the range $20 - 80^\circ\text{C}$. In the ideal case complete de-hydrogenation / cracking will occur leaving a surface layer of adsorbed Carbon, C.

The sensor is held at temperature, T_{ads} , for a time, t_{ads} , during which adsorption of the organic contaminants occurs. The length of time, t_{ads} , is suitably between 10 and 10^5 seconds and is preferably of the order of $10^2 - 10^3$ seconds. Greater sensitivities can be achieved using longer adsorption times. It is, however, desirable that saturation of the measurement electrode during the adsorption phase is avoided as this will change the sticking / reaction probability of the surface, typically surface coverages of < 0.5 monolayers are desirable. In the event that saturation of the electrode occurs this can be overcome by burning the carbonaceous deposit off of the surface of the measurement electrode and re-adsorbing for a shorter period of time.

In the event that incomplete cracking of the hydrocarbon contaminant occurs during the adsorption phase, complete cracking can be achieved by raising the temperature of the sensor to a temperature intermediate that of the adsorption temperature, T_{ads} , and the titration temperature, T_{tit} , and optionally applying a potential V_i across the sensor, under which conditions complete cracking of the adsorbed hydrocarbon occurs. In some applications, V_i may be zero. The sensor is held at the

intermediate temperature for a period of time sufficient to allow complete conversion of any uncracked hydrocarbon contaminant to a carbonaceous deposit on the surface of the measurement electrode.

In the Oxygen titration mode, the sensor temperature is rapidly raised from either the adsorption temperature, T_{ads} , or the intermediate temperature to a fixed absolute temperature, T_{tit} , which is above T_c . During this temperature ramp de-hydrogenated organic material will remain on the surface. Once at T_{tit} a small current I_p is forced to pass through the electrochemical cell, formed between the sensing and reference electrodes and the Oxygen anion conducting electrolyte, pumping Oxygen to the sensing electrode surface, equation 9. Currents of the order of 100 nano-amps to 100 micro-amps are suitably used. The Oxygen progressively combusts the carbonaceous residue on the sensing electrode in accordance with equation 10.



The potential of the sensing electrode, relative to the reference electrode, will tend to the equilibrium thermodynamic value predicted by the Nernst equation, 3, as the titration reaction proceeds. When the equilibrium thermodynamic voltage, V_0 is reached the oxygen titration reaction is complete. The total amount of charge, which has flowed through the cell during the titration reaction is directly proportional to the amount of Oxygen reacted. For the ideal case the amount of carbon accumulated during the adsorption phase will be 1/4 of the total charge, equations 9 and 10. The amount of carbon can be determined from the time taken in the adsorption phase and the surface area of the sensing electrode.

Wet potentiometric titration procedures and cyclic voltammetry are frequently used to monitor the levels of known contaminant species in

solutions. All of these processes take place in the liquid phase and use reversible electrode processes, mostly using water as the major constituent of the solvent and use electrons to directly effect oxidation / reduction. Gas phase electrochemistry is confined to the areas of electrochemical sensors, both potentiometric and amperometric, and solid oxide fuel cells neither of which use any kind of titration reaction.

It will therefore be appreciated that, in contrast to the wet titrametric procedures of the prior art, the sensor of the present invention facilitates the titrametric determination of trace organic contaminants in the gaseous phase using a solid state electrolyte.

Although the sensor of the first aspect of the invention can be used with just two electrodes (the reference and measurement electrode) only, it is preferred to use an electrode arrangement comprising a counter electrode in addition to the measurement and reference electrodes as described above. The counter electrode is positioned adjacent to the reference electrode and in contact with the same reference environment as the reference electrode. In this preferred embodiment, the current I_p flows between the counter electrode and the measurement electrode. The reference electrode therefore provides a constant reference environment from which the electrochemical potentials of both the measurement and counter electrodes and therefore the potential difference across the cell can be determined. The counter electrode is preferably formed from materials such as platinum which catalyse the dissociation of oxygen.

The dimensions of the top and bottom surfaces of the sensor are typically of the order of a few square centimetres or less. The electrodes formed or deposited on each of the surfaces are therefore dimensioned accordingly. The sensing and counter electrodes are each typically of the order of 1cm^2 . The reference electrode is usually of a lesser dimension. The electrodes are typically from about 0.1 to about $50\mu\text{m}$ in thickness.

It will be appreciated that the sensor of the first aspect of the invention can be used to monitor the levels of trace organic contaminants in process environments and a second aspect of the invention provides the use of the sensor according to the first aspect of the invention to monitor levels of trace organic contaminants in process environments.

It will further be appreciated that the sensor of the first aspect of the invention can be used in a method for monitoring the level of trace organic contaminants in process environments. A third aspect of the invention provides a method for monitoring the levels of trace organic contaminants in a monitored process environment, the method comprising the steps of providing an electrochemical sensor comprising:

- a measurement electrode being coated with (or formed from) a catalyst having the ability to catalyse the dissociation of the organic contaminant molecule, the electrode being positioned for exposure to the monitored environment;

- a reference electrode being coated with (or comprised from) a catalyst selected for its ability to catalyse the dissociation of oxygen to oxygen anions, the reference electrode being positioned within a reference environment;

- a solid state oxygen anion conductor disposed between and bridging the measurement and reference electrodes, wherein oxygen anion conduction occurs at or above a critical temperature, T_c ;

- exposing the measurement electrode at a sensor temperature T_{ads} to the monitored process environment containing one or more organic contaminant species for a time t_{ads} thereby to cause the one or more organic contaminant species to be adsorbed onto and dehydrogenate at the surface of the measurement electrode thereby leading to the build up of a carbonaceous deposit at the surface thereof;

- raising the temperature of the sensor to a value T_{ht} above the critical temperature T_c of the solid state oxygen anion conductor and passing a current I_p between the reference electrode and the measurement electrode for a time t_p taken for the potential difference

across the sensor to reach a constant value determined by the equilibrium between the flux of oxygen anions (O^{2-}) arriving at the electrode surface and the rate of desorption of oxygen gas ($O_{2(g)}$) from the electrode surface according to equations 1 and 2;

determining, from the total charge ($I_p t_p$) passed through the sensor at temperature T_{ut} the amount of carbonaceous deposit present at the surface of the measurement electrode and therefore the concentration of organic contaminant species present in the process environment.

The reference environment may, for example, be a gaseous source of oxygen at constant pressure (such as atmospheric air) or a solid-state source of oxygen, typically a metal / metal oxide couple such as Cu / Cu₂O and Pd / PdO or a metal oxide / metal oxide couple such as Cu₂O / CuO.

As indicated above the use of a sensor having reference, counter and measurement electrodes is preferred to optimise the electrical stability across the cell. Therefore, in a second preferred embodiment of the third aspect of the invention there is provided a sensor having, in addition to the reference and measurement electrode as described above, a counter electrode positioned adjacent to the reference electrode and in contact with the same reference environment as the reference electrode. In this preferred embodiment, the current I_p flows between the counter electrode and the measurement electrode. The reference electrode therefore provides a constant reference environment from which the electrochemical potentials of both the measurement and counter electrodes and therefore the potential difference across the cell can be determined.

The invention will now be described with reference to the following figures and examples in which:

Figure 1 illustrates two embodiments of a sensor according to the first aspect of the invention.

Figure 2 illustrates a preferred embodiment of a sensor in accordance with the first aspect of the invention.

Figure 3 illustrates the relationship between the voltage across the cell and the total charge passed there through during the titration time t_p .

Variations on these examples falling within the scope of the current invention will be apparent to a person skilled in the art.

The electrochemical sensor 1 of figure 1a comprises a measurement electrode 2 made of platinum deposited on the upper (sensing) surface 3 of a solid state electrolyte 4 comprising an yttrium stabilised zirconium oxygen anion conductor using techniques such as vacuum sputtering or applying a suitable commercially available "ink" to the surface, for example. In the event that the electrode is formed on the surface of the sensor using an ink, the whole assembly must be fired in a suitable atmosphere determined by the nature of the ink. In use the sensing electrode is exposed to the environment to be monitored and is formed from a material that is able to catalyse the dehydrogenation of a hydrocarbon contaminant such as propylene to carbonaceous material at its surface. A platinum reference electrode 5 is formed on the under surface 6 of the electrolyte 4. The reference electrode is formed on the under surface of the electrolyte 4 using similar techniques to those described above. The reference electrode 4 is placed in contact with a reference environment 7, which may be either a gaseous source of oxygen at constant pressure (such as atmospheric air) or a Solid-state source of oxygen, typically a metal / metal oxide couple such as Cu / Cu₂O and Pd / PdO or a metal oxide / metal oxide couple such as Cu₂O / CuO.

The sensor is typically mounted in the environment to be monitored using a mounting flange 8 and the measurement electrode 2 is typically isolated from the reference electrode 5 through the use of gas tight seals

9. In this way it is possible to separate the environment to be monitored from the reference electrode 5 and the reference environment 7. The solid state electrolyte 4 is provided with a heater and thermocouple arrangement 10 to control the temperature of the sensor. The heater and/or thermocouple may be bonded to the electrolyte prior to the formation of the electrodes; sputtered onto the electrolyte subsequent to the formation of the electrodes or wound round the electrolyte prior to or subsequent to the isolation of the sensing electrodes from the reference and counter electrodes.

A current source is also provided to control the current flowing from the reference electrode to the measurement electrode. A voltmeter is also provided to measure the potential difference across the cell.

In use the sensor is cycled between an adsorption phase and a titration phase. In the adsorption phase, the upper surface of the sensor 1 and therefore the measurement electrode 2 is exposed to an environment to be monitored, including any organic contaminants. The sensor is held at a temperature T_{ads} for a time t_{ads} during which any organic contaminants are adsorbed onto and dehydrogenated at the surface of the measurement electrode 2 resulting in the formation of carbonaceous deposits there at. The sensor then enters the titration phase. The temperature of the sensor is then raised to a temperature T_{tit} above the critical temperature T_c of the electrolyte at which the electrolyte becomes conducting. Once at temperature T_{tit} a known current I_p is passed between the reference electrode 5 and the measurement electrode 2 thereby to force oxygen anions to pass from the reference electrode to the measurement electrode where they are oxidised and react with the carbonaceous deposits formed at the surface of the measurement electrode during the adsorption phase to form carbon dioxide.

During the titration phase the potential difference across the cell is monitored and the time taken for the potential difference to reach a

constant value, V_0 , characterised by the current I_p . The establishment of this constant potential indicates that sufficient oxygen has passed between the reference and measurement electrodes to cause complete oxidation of all the carbonaceous deposits present at the surface of the electrode 2 and therefore that the end point of the oxidative titration has been reached.

By measuring the time taken for all the carbonaceous deposits on the surface of the measurement electrode to be oxidised, it is possible to determine the amount of carbonaceous deposit formed at the surface thereof during the adsorption phase. Since the length of the adsorption phase is known, it is then possible to determine the amount of carbonaceous deposit formed on the surface of the electrode per unit time and from this the concentration of trace organic materials in the process environment.

Figure 2 illustrates another form of sensor according to the invention. The reference numerals refer to the same elements as indicated above, except that the suffix "a" has been added to distinguish the two forms of sensor.

In Figure 3, the change in both the total charge passed through the cell and the measured potential difference across the cell during the passage of such charge over titration time t_{tit} is illustrated. The lower curve represents total charge passed and the upper curve represents potential difference across the cell. It can be seen that as the total charge increases to a maximum value the potential difference across the cell decreases from a maximum value to a minimum constant value. The time taken for the potential difference across the cell to change from the maximum value determined upon application of the current I_p to the cell to the minimum constant value is the time taken for oxidation of all the carbonaceous deposits from the surface of the measurement electrodes.

Examples**Example 1****Construction of the Sensor**

Reference, sensing and optionally counter electrodes were formed on a thimble / disc of the oxygen anion conducting electrolyte (commercially available from various suppliers) by sputtering under vacuum or using commercially available 'inks' and firing the assembly in a suitable atmosphere according to the procedure given by the ink manufacturer.

A gas tight seal (resistant to both vacuum and pressure) was formed around the oxygen anion conducting electrolyte to isolate the sensing electrode from the reference electrode and optionally counter electrode using standard procedures. Depending upon how the sensor is to be heated the heater / thermocouple can be added at any appropriate stage during manufacture.

Example 2**Determination of the TOC levels in a Process Gas**

A sensor having a YSZ solid state electrolyte having a T_c of 300°C and a platinum measurement electrode with a surface area (A) of 1cm^2 , the electrode having a surface density, ρ , of 10^{15} atoms/ cm^2 was exposed to a process gas containing propylene at a temperature of T_{ads} for a time t_{ads} of 10^3 seconds. The average sticking probability, S , for organic contaminants on the sensing electrode is 0.1. The temperature of the sensor was raised to T_{tit} and a current I_p of 2×10^{-6} A was passed between the reference and measurement electrode. During the passage of the current the potential difference across the cell dropped to a constant value of 350mv over a period t_{tit} of 100 seconds. The total charge passed between the reference and measurement electrode was thus 2.10^{-3} Coulombs which corresponds to the formation of 0.3 monolayers of carbonaceous deposit in accordance with Equation 11.

$$M = \frac{I_{std}}{4\pi} \frac{1}{A\rho}$$

Equation 11

The total equivalent partial pressure (mb) of the organic contaminant (expressed as equivalents of carbon atoms) is calculated as 1.0×10^{-8} mb or 1.0 ppt using equations 12, 13.

$$P_{TOC} = \frac{M}{S_{std}} \times 3.4 \times 10^{-6} \quad \text{Equation 12}$$

$$TOC_{(ppt)} = P_{TOC} \times 10^{-9} \quad \text{Equation 13}$$

Claims

1. An organic contaminant molecule sensor, for use in a low oxygen concentration monitored environment the sensor comprising an electrochemical cell having:

a measurement electrode being coated with (or formed from) a catalyst having the ability to catalyse the dissociative adsorption of the organic contaminant molecule, the electrode being positioned for exposure to the monitored environment;

a reference electrode being coated with (or comprised from) a catalyst selected for its ability to catalyse the dissociation of oxygen to oxygen anions, the reference electrode being positioned within a reference environment;

a solid state oxygen anion conductor disposed between and bridging the measurement and reference electrodes, wherein oxygen anion conduction occurs at or above a critical temperature, T_c ;

means for controlling and monitoring the temperature of the cell, and sealing means for separating the reference environment from the monitored environment; and

means for controlling the electrical current (I_p) flowing between the reference and measurement electrodes

whereby at temperatures (T_{ads}) below the critical temperature, T_c , organic contaminant molecules are adsorbed onto and dissociated at the surface of the measurement electrode leading to the build up of carbonaceous deposits at the surface thereof and at temperatures (T_{ox}) above the critical temperature (T_c), an electrical current (I_p) is passed between the reference and measurement electrode thereby to control the number of oxygen anions passing from the reference electrode to the measurement electrode to oxidise the carbonaceous deposits formed at the surface thereof and the formation of carbon dioxide.

2. A sensor according to claim 1, wherein the measurement electrode is coated with or formed from an element selected from the group comprising rhenium, osmium, iridium, ruthenium, rhodium, platinum and palladium and alloys thereof.
3. A sensor according to claim 2, wherein the alloys used further include alloys including one or more elements selected from silver, gold and copper.
4. A sensor according to any one of claims 1 to 3, wherein the reference electrode is able to catalyse the dissociation of oxygen.
5. A sensor according to claim 4, wherein the reference electrode is selected from platinum, palladium or other metal able to dissociatively adsorb oxygen or any alloy thereof.
6. A sensor according to any one of the preceding claims, wherein the solid state oxygen anion conductor is selected from gadolinium doped ceria and yttria stabilised zirconia.
7. A sensor according to any one of the preceding claims, which further comprises a counter electrode, said counter electrode being positioned adjacent to the reference electrode.
8. A sensor according to claim 7, wherein the counter electrode is selected from platinum, palladium or other metal able to dissociatively adsorb oxygen.
9. A sensor according to any of the preceding claims, wherein the reference environment is a gaseous source of oxygen at atmospheric pressure, optionally atmospheric air.

10. A sensor according to any of claims 1 to 8, wherein the reference environment comprises a solid-state source of oxygen.
11. A sensor according to claim 10 wherein the solid state source is selected from a metal / metal oxide couple (optionally Cu / Cu₂O or Pd / PdO), or a metal oxide /metal oxide couple (optionally Cu₂O / CuO).
12. A sensor according to any one of the preceding claims, wherein the means for controlling or monitoring the temperature of the cell comprises a heater and thermocouple arrangement.
13. A sensor according to any preceding claim further including means for providing a potential across the sensor.
14. Use of a sensor according to any one of claims 1 to 13 for monitoring the levels of trace organic contaminants in a low oxygen concentration monitored process environment.
15. A method for monitoring the levels of trace organic contaminants in a monitored process environment, the method comprising the steps of providing an electrochemical sensor comprising:
 - a measurement electrode being coated with (or formed from) a catalyst having the ability to catalyse the dissociation of the organic contaminant molecule, the electrode being positioned for exposure to the monitored environment;
 - a reference electrode being coated with (or comprised from) a catalyst selected for its ability to catalyse the dissociation of oxygen to oxygen anions, the reference electrode being positioned within a reference environment;
 - a solid state oxygen anion conductor disposed between and bridging the measurement and reference electrodes, wherein

oxygen anion conduction occurs at or above a critical temperature, T_c ;

exposing the measurement electrode at a sensor temperature T_{ads} to the monitored process environment containing one or more organic contaminant species for a time t_{ads} thereby to cause the one or more organic contaminant species to be adsorbed onto and dehydrogenate at the surface of the measurement electrode thereby leading to the build up of a carbonaceous deposit at the surface thereof;

raising the temperature of the sensor to a value T_{tit} above the critical temperature T_c of the solid state oxygen anion conductor and passing a current I_p between the reference electrode and the measurement electrode for a time t_p taken for the potential difference across the sensor to reach a constant value determined by the equilibrium between the flux of oxygen anions (O^{2-}) arriving at the electrode surface and the rate of desorption of oxygen gas ($O_{2(g)}$) from the electrode surface according to equations 1 and 2;

determining, from the total charge ($I_p t_p$) passed through the sensor at temperature T_{tit} the amount of carbonaceous deposit present at the surface of the measurement electrode and therefore the concentration of organic contaminant species present in the process environment.

16. A method according to claim 15, which further comprises the step of heating the sensor to a temperature intermediate the adsorption temperature, T_{ads} , and the titration temperature, T_{tit} , subsequent to the adsorption step to facilitate the complete conversion of any uncracked hydrocarbon contaminant to a carbonaceous deposit on the surface of the measurement electrode and thereafter raising the temperature of the sensor to the titration temperature, T_{tit} .
17. A method according to claim 15 or 16, in which the adsorption temperature is in the range 20 to 150°C.

18. A method according to any one of claims 15 to 17, in which the adsorption time is in the range 10^2 to 10^5 seconds.
19. A method according to claim 18, wherein the adsorption time is of the order of 10^4 seconds.
20. A method according to any one of claims 15 to 19, wherein the titration temperature of the sensor is in the range 300 to 600°C.
21. A method according to any one of claims 15 to 20, wherein the current I_p passing between the reference and measurement electrode is in the range 10nA to 100µA.
22. A method according to any one of claims 15 to 21, wherein the sensor is further provided with a counter electrode adjacent to the reference electrode.
23. A method according to any one of the claims 15 to 22, wherein the reference environment is a gaseous source of oxygen at atmospheric pressure, optionally atmospheric air.
24. A method according to any one of the claims 15 to 22, wherein the reference environment comprises a solid-state source of oxygen.
25. A method according to claim 24 wherein the solid state source is selected from a metal / metal oxide couple (optionally Cu / Cu₂O or Pd / PdO), or a metal oxide / metal oxide couple (optionally Cu₂O / CuO).
26. A method according to any one of claims 15 to 25 further including the step of applying a potential V_i across the sensor.

28

27. An organic contaminant molecule sensor substantially as described herein and with reference to the accompanying Figures.
28. A method for monitoring the levels of trace organic contaminants in a monitored process environment substantially as described herein.

ABSTRACT**Electrochemical Sensor**

The invention provides an organic contaminant molecule sensor, for use in a low oxygen concentration monitored environment the sensor comprises an electrochemical cell having:

a measurement electrode being coated with (or formed from) a catalyst having the ability to catalyse the dissociative adsorption of the organic contaminant molecule, the electrode being positioned for exposure to the monitored environment;

a reference electrode being coated with (or comprised from) a catalyst selected for its ability to catalyse the dissociation of oxygen to oxygen anions, the reference electrode being positioned within a reference environment;

a solid state oxygen anion conductor disposed between and bridging the measurement and reference electrodes, wherein oxygen anion conduction occurs at or above a critical temperature, T_c ;

means for controlling and monitoring the temperature of the cell, and sealing means for separating the reference environment from the monitored environment; and

means for controlling the electrical current (I_p) flowing between the reference and measurement electrodes

whereby at temperatures (T_{ads}) below the critical temperature, T_c , organic contaminant molecules are adsorbed onto and dissociated at the surface of the measurement electrode leading to the build up of carbonaceous deposits at the surface thereof and at temperatures (T_{tit}) above the critical temperature (T_c), an electrical current (I_p) is passed between the reference and measurement electrode thereby to control the number of oxygen anions passing from the reference electrode to the measurement electrode to oxidise the carbonaceous deposits formed at the surface thereof and the formation of carbon dioxide.

(Fig. 1)

1/2

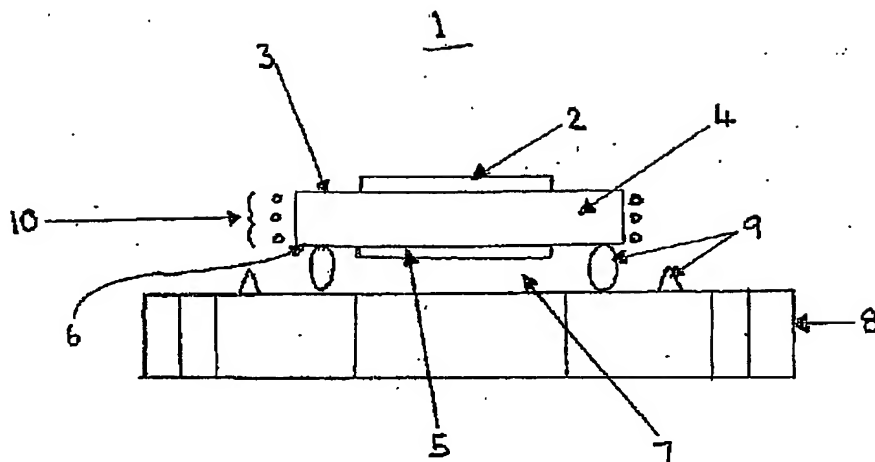


FIG. 1

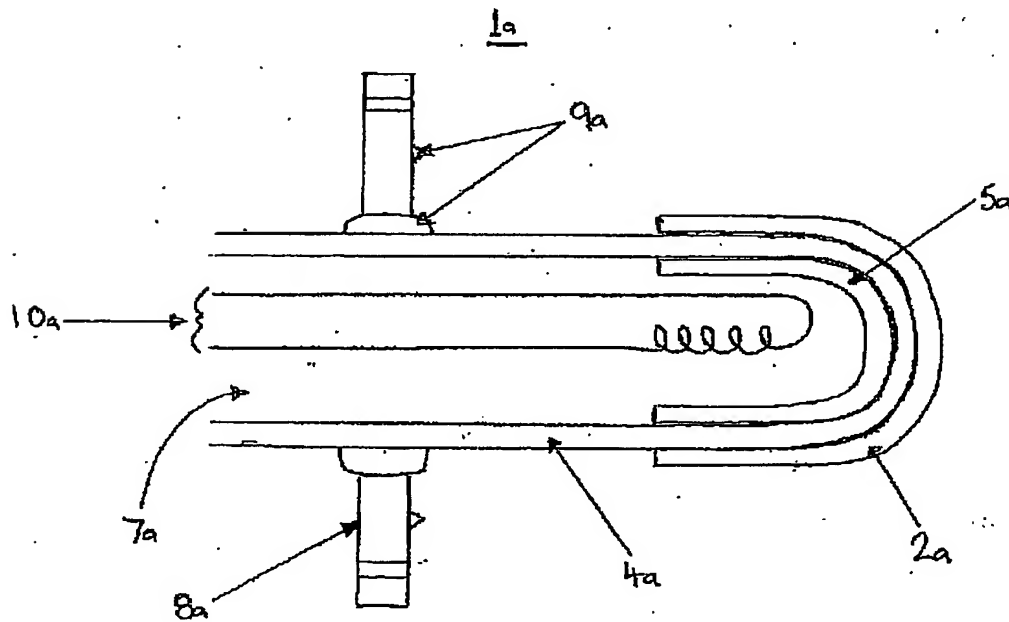


FIG. 2

2/2

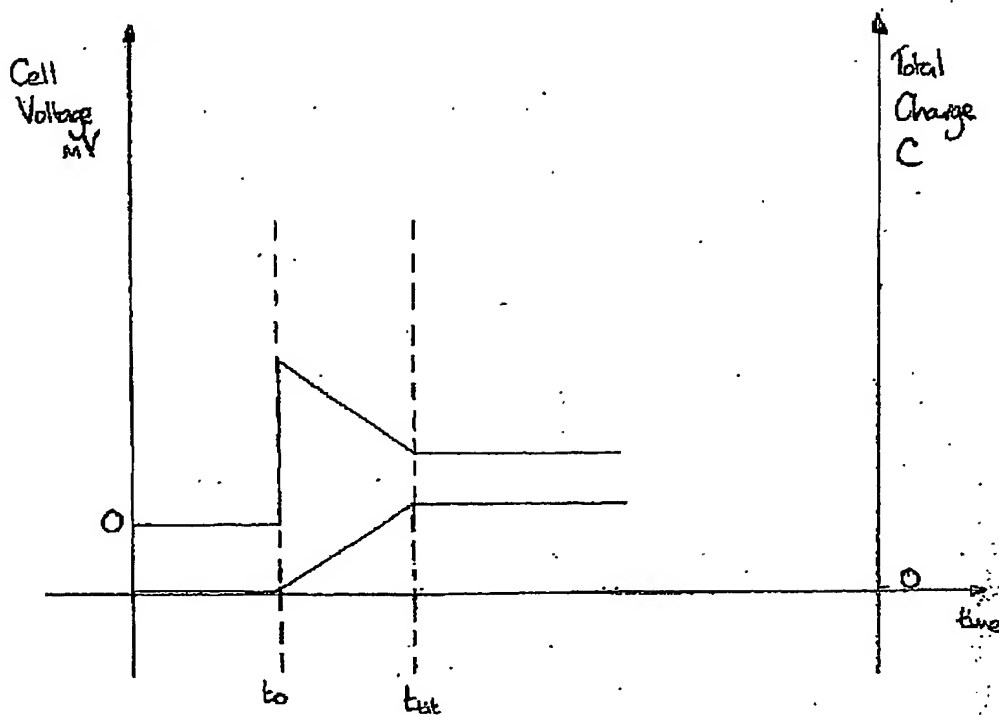
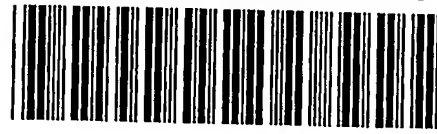


FIG. 3

PCT/GB2004/003370



**This Page is Inserted by IFW Indexing and Scanning
Operations and is not part of the Official Record**

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- ☐ **BLACK BORDERS**
- ☐ **IMAGE CUT OFF AT TOP, BOTTOM OR SIDES**
- ☐ **FADED TEXT OR DRAWING**
- ☐ **BLURRED OR ILLEGIBLE TEXT OR DRAWING**
- ☐ **SKEWED/SLANTED IMAGES**
- ☐ **COLOR OR BLACK AND WHITE PHOTOGRAPHS**
- ☐ **GRAY SCALE DOCUMENTS**
- ☐ **LINES OR MARKS ON ORIGINAL DOCUMENT**
- ☐ **REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY**
- ☐ **OTHER:** _____

IMAGES ARE BEST AVAILABLE COPY.

As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.